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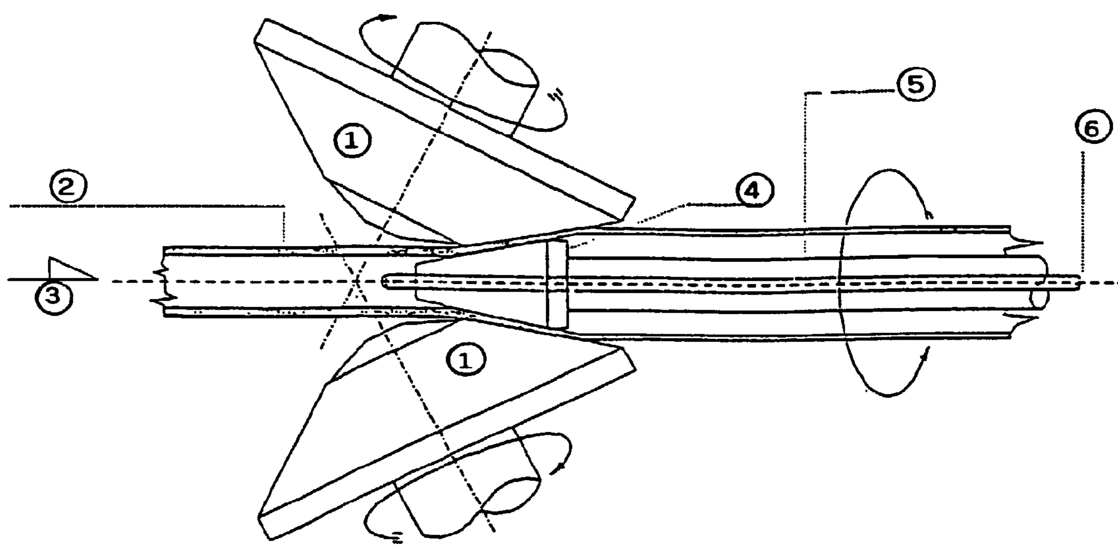
(54) **Title:** MARTENSITIC STAINLESS STEEL AND SEAMLESS STEEL PIPES PRODUCED WITH IT



(57) **Abstract:** Martensitic stainless steel with high resistance to corrosion, consisting of the following ingredients: Mn from 0.1 % to 0.3 %, P ≤ 0.02 %, S ≤ 0.002 % Cr from 10 % to 13 %, C ≤ 0.02 wt%, Si from 0.1 % to = 0.3 wt%, Ni from 5 % to 8 %, Mo from 1.5 % to 3 %, N ≤ 0.02 % and use of the above-mentioned steel in the fabrication of seamless steel pipes with diameters of up to 28'', with a process of rotary-expansion rolling.

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— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

MARTENSITIC STAINLESS STEEL AND SEAMLESS STEEL PIPES PRODUCED WITH IT

Scope of the invention

The invention regards the production of a martensitic stainless steel and its use in the fabrication of seamless steel pipes of large dimensions, with excellent weldability, that are suitable for use in pipelines in a corrosive environment owing to the presence of wet carbon acid gas and wet hydrogen sulphide gas at a very high pressure and at a temperature of up to 150°C and over.

The invention also regards the fabrication of the aforesaid pipes using a process of rotary-expansion hot rolling.

Brief description of the drawings

In Figure 1:

❶ = pair of conical rolls with axes of rotation not co-planar either between them or with respect to the longitudinal axis of the rolling mill.

❷ = incoming master pipe

❸ = direction of rolling

❹ = expanding mandrel

❺ = mandrel-holder shaft

❻ = pipe for fluid for deoxidation of the internal surface

In Figure 2:

❶ = furnace for heating master pipes

❷ = rotary rolling mill of Figure 1

❸ = pair of oblique rolls with axial mandrel for surface finishing.

❹ = subsequent heating furnace

❺ = pairs of rolls for calibration of pipe

❻ = cooling.

Detailed description of the invention

The present invention regards the fabrication of seamless steel pipes of large dimensions, with external diameters larger than 16" and up to 28", suitable for use in pipelines where a high mechanical resistance is required, as well as excellent weldability and resistance to corrosion in severe conditions, such as those occurring with fluids owing to the simultaneous presence of CO_2 and H_2S and

water, as well as chlorides (e.g., NaCl) at temperatures of up to 150°C.

The extraordinarily high performance of the products forming the subject of the invention are due to the use in their fabrication of a martensitic stainless steel which represents an essential aspect of the invention. In addition to presenting exceptional resistance to corrosion as mentioned above, the said steel can readily be hot processed at over 1000°C and up to 1200°C. In particular, it is suitable for the fabrication of seamless steel pipes of large dimensions, with external diameters of up to 28" in a rotary-expansion hot-rolling mill equipped with conical rolls and with an axial mandrel.

The martensitic stainless steel forming the subject of the invention

In the last few years, there has been an increasing demand for tubing for pipelines made of steels that are resistant to extremely severe conditions of corrosion which include the simultaneous presence of H_2S and CO_2 in the presence of H_2O and temperatures of over 100°C and up to 150°C, at very high pressures.

Amongst the known steels presenting corrosion resistance in the severe conditions referred to above, there are those with 0.2% C and 13% Cr, which, however, have poor weldability and require a preliminary heat treatment and a subsequent treatment at high temperature to prevent fissuring of the welds.

Better performance has been achieved with high-chromium steels (22-25% Cr), but at the expense of a sharp increase in the cost of the steel.

A martensitic stainless steel has now been obtained with excellent weldability and workability at high temperatures in the 1100 to 1200°C range, high resistance to corrosion from CO_2 + H_2S in the presence of H_2O and also of chlorides. The pipes made of this steel present a very high resistance to pressure.

The steel according to the invention contains:

Formulation 1

C ≤ 0.02 wt%, Si from 0.1% to 0.3 wt%

Mn from 0.1% to 0.3 wt%

P ≤ 0.02 wt% S ≤ 0.002 wt%

Cr from 10% to 13 wt% Ni from 5% to 8 wt%

Mo from 1.5% to 3 wt% N ≤ 0.02 wt%

with (C + N) = from 0.02% to 0.04 wt%.

The rest up to 100% consisting basically of Fe.

Formulation 2

As for Formulation 1, but also containing:

from 0.1 to 2% wt of W

with (C + N) = from 0.02% to 0.04% by weight

Formulation 3

As for Formulation 1, but also containing:

from 0.01 to 0.1% of Ti and/or from 0.01 to 0.1% of Nb

with (C + N) = from 0.02% to 0.04%

Formulation 4

As for Formulation 1, but also containing from 0.1 to 2% wt of W and from 0.01% to 0.1% of Ti and/or Nb.

The stainless steel according to the present invention has been obtained, adopting the following criteria:

Carbon

Carbon increases the mechanical resistance following upon the formation of chromium carbide, but decreases the resistance to corrosion following upon the reduction of free Cr. The carbon content indicated (≤ 0.02%) in combination with the condition of (C + N) comprised between 0.02% and 0.04% in practice represents an excellent compromise.

Silicon

Silicon, from 0.1% to 0.3%, functions as a deoxidizer: below 0.1% it does not achieve any appreciable effect; above 0.3% it causes crystallization of δ ferrite, and an increase in Ni is required to reduce the ferritic structure in favour of the martensitic one. Taking into account also the high cost of nickel, a limit value of Si of 0.3% has been established.

Manganese

A manganese content of 0.1 to 0.3% also functions as deoxidizer; it has no significant effect below 0.1%. The hot workability is reduced. Above 0.3%, corrosion due to CO_2 + H_2S increases.

Phosphorus

Phosphorus ≤ 0.02%. The limit of 0.02% has been fixed to maintain excellent hot

workability without any detriment to corrosion resistance.

Sulphur

Sulphur ≤ 0.002%. Low sulphur content does not contribute to increasing the resistance to corrosion but safeguards the high hot workability.

Chromium

Chromium content of 10% to 13%. A minimum of 10% improves the resistance to corrosion due to CO_2 + H_2O. In lower quantities the improvement in regard to corrosion is practically insignificant. It promotes ferritic crystallization at the expense of the martensitic structure; for this reason, it has been limited to 13%, at the same time adding also nickel, which promotes the martensitic structure.

Nickel

Nickel content of 5% to 8%. For an advantageous promotion of the martensitic structure, at least 5% is used. Taking into account the high cost of nickel, a content of 5% to 8% is considered optimal.

Molybdenum

Molybdenum content of 1.5% to 3%. Molybdenum improves resistance to corrosion but is not effective below 1.5%: it promotes the ferritic structure at the expense of the martensitic structure. If it exceeds 3%, it is necessary to add further nickel to safeguard the martensitic structure. Consequently, the maximum content is fixed at 3%.

Nitrogen

N ≤ 0.02%. Nitrogen, by forming compounds with Cr (nitrides), increases the mechanical resistance, but if added in excess reduces the resistance to corrosion. In addition, amounts exceeding the limit set may give rise to high hardness in welding (heat-affected zone) and render necessary a post-welding heat treatment. The amount indicated (≤0.02%) in combination with the (C + N) condition comprised between 0.02% and 0.04%, in practice represents an optimal compromise.

Tungsten

Tungsten (at 0.1% to 2% by weight) increases the resistance to corrosion, as well as mechanical resistance. Below 0.1%, the improvement is insignificant; above 2%, the hot workability is reduced. The 0.1 to 3% range represents an

optimal content for both.

Titanium and Niobium

Both titanium and niobium, in small quantities between 0.01% and 0.1%, improve the mechanical resistance and the toughness of the steel (they form carbides with the carbon present in the steel, in this way refining the crystal grain). Above 0.1%, there is oversaturation.

Carbon + Nitrogen

The (C + N) condition of 0.02% to 0.04% represents a compromise to obtain sufficient mechanical resistance without increasing excessively the hardness in the heat-affected zone as a result of welding (with consequent need for post-heat treatment).

Method and device for the fabrication of the seamless steel pipes forming the subject of the invention

The martensitic stainless steel described above constitutes the specific material necessary for the fabrication of seamless steel pipes of large dimensions, obtained according to a process and the corresponding device developed by the present applicant. The rolling device defined as rotary-expansion rolling device, is schematically represented in Figure 1, from which the working principle can be deduced.

The rotation axes of the rolls being "skew" have a minimal distance between them of about 160 mm. The rolls are further characterised by their geometrical structure consisting of an entrance conus having conicity angle of about 56° (i.e. vertex angle 56° x 2 = 112°) and a base conus having conicity angle of about 46°.

The rotation axes of the conical rolls form an angle of about 60° with a straight line parallel to the longitudinal axis of rolling mill.

The conical rolls exert on the pipe being processed an axial thrust in the direction of advance, as well as a rotation: the pipe thus assumes a helicoidal motion. The incoming material then undergoes a transverse rolling with expansion.

The position of the expanding mandrel is controlled by means of the shaft (5) operated by a hydraulic device.

Thus the correct thickness of the walls of the rolled pipe is assured through the adjustment under load during the rolling process, of the position of the mandrel-

holder shaft (for example by hydraulic capsules).

The increase in the diameter of the pipe with a single rolling pass can arrive at 70%, with corresponding reduction of the thickness of the walls of the pipe.

Rolling is carried out with a temperature of the material being processed of between 1150° and 1200°C.

Figure 2 illustrates the accessory devices of the rotary-expansion rolling apparatus shown in Figure 1.

The method and corresponding equipment proposed make it possible to obtain, with the use of the martensitic stainless steel according to the invention, pipes of large diameters (up to 28") presenting excellent surface characteristics.

Examples

Some types of martensitic stainless steel according to the invention are given in Table 1. The last three types (Tests J, K and L) were prepared for carrying out comparison tests.

Table 2 gives the assessments on the basis of the tests carried out on the steels of Table 1.

In particular, as regards the workability at high temperature, the comparison steels (Specimens J, K and L) were poor and hence not suitable for the fabrication of the pipes according to the process and using the rolling device according to the present invention. It is to be noted that the above-mentioned comparison specimens do not satisfy, as regards their composition, the requisites established for the present invention; namely, the specimen J has an excessive content of P (0.038% instead of 0.020), whilst the specimens K and L have an excessive content of sulphur. (0.004% instead of 0.002%).

TABLE 1

Example No.	Chemical composition (wt%)													notes
	C	Si	Mn	P	S	Cr	Ni	Mo	N	W	Ti	Nb	C+N	
A	0.013	0.22	0.27	0.011	0.002	12.6	7.3	2.3	0.012	-	-	-	0.025	Invention
B	0.011	0.28	0.15	0.012	0.001	10.8	5.4	2.7	0.016	-	-	-	0.027	Invention
C	0.008	0.15	0.24	0.015	0.001	11.6	7.6	2.5	0.018	1.8	-	-	0.026	Invention
D	0.016	0.20	0.21	0.012	0.001	12.3	6.2	1.8	0.008	-	0.02	-	0.024	Invention
E	0.012	0.18	0.23	0.005	0.001	11.8	5.7	1.9	0.016	-	-	0.05	0.028	Invention

Example No.	Chemical composition (wt%)													notes
	C	Si	Mn	P	S	Cr	Ni	Mo	N	W	Ti	Nb	C+N	
F	0.011	0.20	0.26	0.019	0.001	11.7	5.8	2.2	0.016	0.4	0.03	0.04	0.027	Invention
G	0.013	0.26	0.18	0.038	0.002	9.3	5.6	2.0	0.015	-	-	-	0.028	Comparison
H	0.011	0.29	0.20	0.008	0.004	12.4	5.3	2.6	0.014	-	-	-	0.025	Comparison
I	0.018	0.14	0.29	0.021	0.004	11.7	6.2	1.9	0.008	-	-	-	0.026	Comparison

Notes: Example J: excessive phosphorus (max. 0.02%)

Examples K, L: excessive sulphur (max. 0.002%)

TABLE 2

Example	Hot workability	Resistance to surface corrosion	SSC test	Weldability	Overall assessment	Notes
A	O	O	O	O	O	Invention
B	O	O	O	O	O	Invention
C	O	O	O	O	O	Invention
D	O	O	O	O	O	Invention
E	O	O	O	O	O	Invention
F	O	O	O	O	O	Invention
G	O	O	O	O	O	Invention
H	O	O	O	O	O	Invention
I	O	O	O	O	O	Invention
J	X	O	O	O	X	Comparison Example
K	X	O	O	O	X	Comparison Example
L	X	O	O	O	X	Comparison Example

O = good

X = poor

CLAIMS

1. A martensitic stainless steel suitable for the fabrication of seamless steel pipes with high resistance to corrosion, consisting of the following ingredients:
Mn from 0.1% to 0.3%, P≤ 0.02%, S≤ 0.002% Cr from 10% to 13%,
C ≤ 0.02 wt%, Si from 0.1% to = 0.3 wt%,
Ni from 5% to 8%, Mo from 1.5% to 3%, N≤ 0.02%
and in which C + N = from 0.02% to 0.04%.
The rest up to 100% basically consisting of Fe.

2. A martensitic stainless steel according to Claim 1, but also containing from 0.1% to 2% of W.

3. A martensitic stainless steel according to Claim 1, but also containing from 0.01% to 0.1% of Ti and/or from 0.01% to 0.1% of Nb.

4. A martensitic stainless steel according to Claim 1, but also containing from 0.1% to 2% of W and from 0.01% to 0.1% of Ti and/or Nb.

5. Pipes made of martensitic stainless steel suitable for being used for pipelines, having high resistance to corrosion from CO_2 + H_2S in the presence of water and/or saline solutions, at high temperatures, made without seams using a rolling method, with the use of steel according to Claims 1-4.

6. A process for the fabrication of the pipes according to Claim 5, in which a rotary-expansion rolling process is carried out, where the material is processed at temperatures of between 1150° and 1200°C, said process being characterized by the rolling device schematically represented in Figure 1 and comprising a pair of conical rolls 1, an expanding mandrel 4 mounted on the shaft 5, and in which the conical rolls 1 having rotation axes not complanar either between them or with respect to the longitudinal axis of the rolling mill impart a helicoidal motion on the incoming master pipe undergoing rolling.

7. Process according to claim 6 wherein the rotary rolling mill is further characterised by the fact that the minimal distance between the rotation axes of the two rolls is about 160 mm and that the rotation axes form and angle of about 60° with a straight line parallel to the longitudinal axis of the rolling mill.

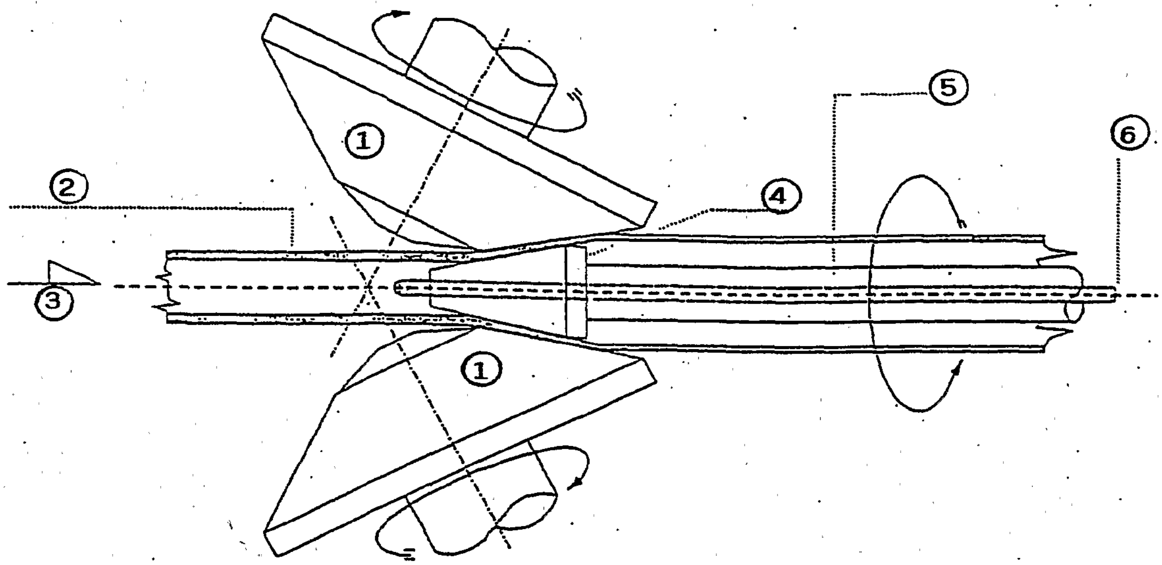

FIGURE 1

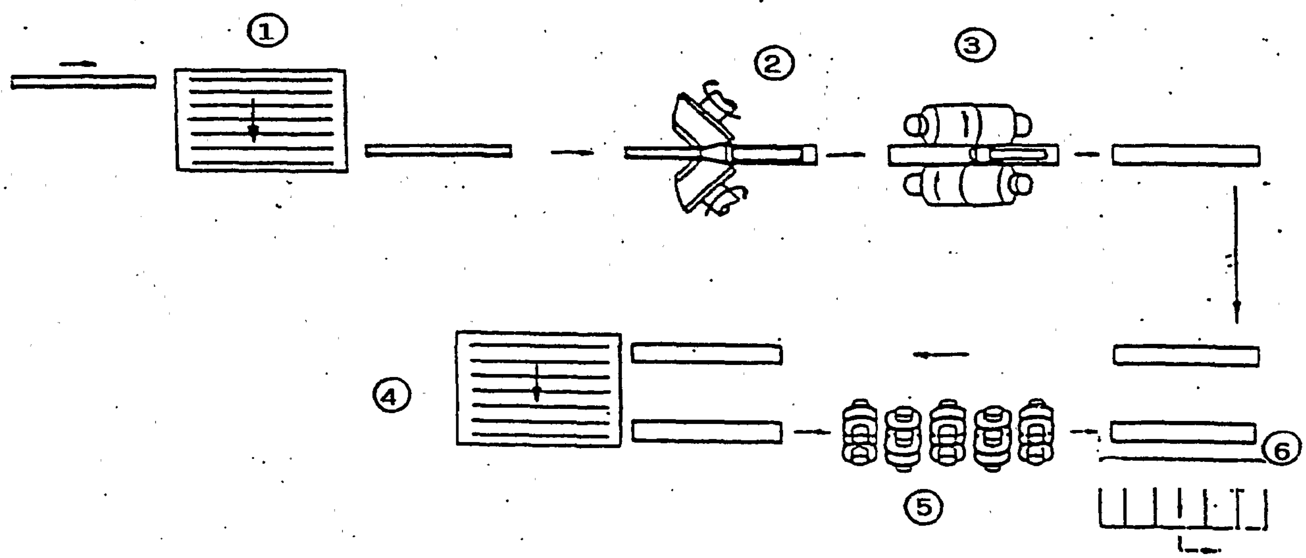

FIGURE 2

INTERNATIONAL SEARCH REPORT

Inte al Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C21D9/08 C22C38/44 B21B17/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C21D C22C B21B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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